Integration of Reduced Graphene Oxide and Au-Pt Nanoparticles Fabricated by Femtosecond Laser Pulse Irradiation

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論 文 内 容 要 旨

In a decade ago, graphene became a rising star in material science community due to its superior electrical, mechanical, thermal and optical properties for applications such as electronic devices, filtration, energy storage and so on. Many efforts have been devoted to the large-scale graphene production to respond to the high expectations from industry. Several approaches of graphene synthesis have been proposed in the last ten years. Chemical vapor deposition (CVD), epitaxial growth on silicon carbide (SiC) and carbon nanotube unzipping were developed to produce high quality graphene with moderate productivity. However, these methods have drawbacks with regard to cost and complexity of the process. Reduction of graphene oxide (GO) is also included in the approach of graphene synthesis. Similarity of their basal structure between GO and graphene stimulates researchers to utilize GO as a suitable precursor for graphene mass production or as a support of composite materials. Even though the quality of final product is relatively low due to the high defect density on the basal plane of a graphene sheet, the utilization of GO as a precursor of graphene synthesis has several advantages especially in high scalability and low cost production. In addition, GO has higroscopicity and good dispersity in aqueous solution because it contains a lot of oxygen groups on its basal plane, which facilitates a simple and low-cost wet processing in aqueous solution. The important point in research and application of GO for graphene-like material synthesis is reduction process that can recover the structure and the property of graphene as much as possible. Chemical method, thermal method and their combination are favorite routes to reduce GO, since they can produce highly reduced graphene oxide (rGO) with high carbon-oxygen (C/O) ratio. However, these methods have drawbacks such as low purity and increase of defect site density on the basal plane due to the usage of chemical agents and harsh condition during the process. Recently, several groups proposed photoreduction methods to avoid impurities and to maintain defect sites on the basal plane. One of methods is to use femtosecond (fs) laser pulse irradiation. In this thesis, I proposed utilization of fs laser pulse irradiation as a potential method in rGO preparation, metal nanoparticle

fabrication and composite material production. Consequently, controlled reduction of GO was performed using fs laser irradiation in aqueous solution. The main goal of the study was to obtain the basic understanding of GO reduction in aqueous solution using fs laser irradiation, effect of flow rates and repetition rates towards the improvement of nanoparticle (NP) productivity and stability, and finally the formation of hybrid material of rGO and NPs with nano-GO used as a capping agent. Lastly, catalytic performance of synthesized composite materials, NPs/rGO, was measured to examine the effectiveness of the proposed method. This study is also devoted to show advantages of the proposed method compared to other techniques.

Femtosecond laser pulse irradiation for the formation of rGO is a versatile technique because many types of samples in the form of solid and solution are applicable. Nowadays, femtosecond laser pulses have been applied for the fabrication of micro/nano-circuits with high electrical conductivity in electronic devices because complex pattern formation with high resolution is possible. However, the availability of using fs laser for the improvement of rGO quality in solution is not well known. A few experimental and theoretical studies have shown potencies of utilizing fs laser. Interaction between femtosecond laser pulse and material can suppress thermal diffusion in the surrounding region remarkably reducing thermal effects such as melting, re-solidification, formation of cracks around the irradiation area. On the other hand, laser irradiation of aqueous solution can lead to optical breakdown of water molecules as a result of multi-photon absorption and avalanche photoionization processes. Namely, high laser intensity more than 1 TW/cm^2 is possible to be produced by tightly focusing femtosecond laser pulse resulting in optical breakdown of water molecules. Accordingly, several transient reactive species such as solvated electron (e^-_{aq}), hydrogen radicals ($H^\bullet$) and hydroxyl radicals ($OH^\bullet$) are produced. Especially, e^-_{aq} and $H^\bullet$ play an essential role in the reduction of GO and metal ions into rGO and metal NPs, respectively, because they act as reducing agents due to having negative reduction potential (-2.87 VSHE). Reduction mechanism of GO in solution by intense fs laser pulse irradiation has similarity with synthesis of metal or alloy NPs in aqueous solution. This fact opens a possibility of composite synthesis of both materials in aqueous media. In this thesis, the work is divided into three main parts. The first one is to look for optimum laser condition to get highly reduced GO, which would be used for the formation of catalyst for practical application of rGO. After that, an attempt to increase productivity of metal nanoparticles is performed by introducing a simple flow system. Lastly, combination of rGO as a catalyst support and metal or alloy nanoparticles as a catalyst for methanol oxidation reaction is tested. Innovative approach using nano-scale GO is introduced as a capping agent for the first time. For getting fully understanding on the samples before and after laser irradiation, spectroscopy, microscopy, and X-ray diffraction techniques are used to characterize samples. In addition, four-point probe and cyclic voltammetry techniques are used to determine electrical property and catalytic performance of synthesized material.

The objective of the first part is to determine optimum fs laser condition to reduce GO efficiently. As briefly noted in the thesis, GO contains several types of oxygen groups. Hydroxyl and epoxy groups are mostly located on the basal plane while carbonyl, carboxyl and ester groups are located at the edge of the plane. Electrical properties of rGO are greatly influenced by restoration

of carbon double-bond networks on the basal plane. Therefore, selecting appropriate laser power is essential not only to eliminate oxygen groups on the basal plane and restoring the sp^2 hybridization, but also to reduce the defect density on it. To achieve the objectives, different conditions of laser fluence and irradiation time were verified for the reduction of GO in solution. At first, the effect of laser fluence on the reduction of rGO was investigated by applying different laser fluences from 10 mJ/cm^2 to 140 mJ/cm^2 with constant irradiation time of 60 minutes. From the UV spectra of the solutions after irradiation, 80 mJ/cm^2 was the optimum laser fluence because it showed the largest red shift of the absorption peak compared to that obtained by GO standard. Higher laser fluences than 80 mJ/cm^2 were not effective to reduce GO. Increasing hydrogen peroxide (H_2O_2) concentration in rGO suspension by photo-oxidation of water by laser irradiation was suggested by the blue-shift of the absorbance peak. This was confirmed by applying titanium (IV) sulfate solution, which generates a complex compound with peroxide giving intense yellow color. After that, the optimum irradiation time was investigated by applying different irradiation times with a constant laser fluence of 80 mJ/cm^2. From this step, 120 minutes irradiation time was decided to be optimum. The structure and property of rGO formed by fs laser irradiation were characterized using several analytical methods. X-ray diffraction (XRD) indicated that the interplanar spacing of graphene layers was decreased from 9.81 Å to 3.5 Å, which is close to that of pristine graphite, by fs laser irradiation in the optimal condition. From this data, it could be concluded that fs laser pulse can eliminate oxygen functional groups effectively. In addition, elemental composition was determined using X-ray photoelectron spectroscopy (XPS). GO has three spectrum corresponding to C=C, C-O and C=O bonds. The intensity of C-O bonds decreased gradually compare to C=C bonds, while C=O bond was relatively constant during irradiation. By applying the optimum condition, C-O bonds disappeared and changed into C=C and C-C bonds. As a result, the carbon content (C/O) increased from 1.1 to 7.4. Furthermore, Raman spectroscopy of GO and rGO samples showed two clear bands, namely D and G band. Every Raman spectra showed similar Raman shift implying no distortion in the lattice structure was produced during GO reduction by fs laser. Intensity ratio of D and G bands is associated with defects and graphitic densities on the graphene sheet. The intensity ratio of D/G bands was decreased to 20 %, depending on irradiation time, which was different from rGO by chemical and thermal methods. Lastly, electrical property was measured by four-point probe technique. The sheet resistivity of rGO by fs laser irradiation in the optimal condition was greatly decreased 1800 times compared to that of GO standard.

My second study focused on increasing NPs productivity for practical application using highly intense femtosecond laser irradiation. Using this method, solid-solution alloy NPs of noble metals can be easily synthesized in the mixed metal ion solution, even though these mixtures are immiscible nature in a multi-metallic system. The proposed method has advantages compared to conventional chemical and physical NPs synthesis methods due to simplicity, purity, and controllability of alloy composition of the synthesized NPs. To improve NPs productivity, I proposed a simple flow system, in which metal ion solution is circulated by a pump in a closed system. Increasing reactor size can increase the batch capacity. The effect of

irradiation time, repetition rate, and flow rate on the particle profiles, productivity and stability were studied. Using transmission electron microscopy (TEM), irregular shaped particles with large mean particle size were observed for 30 minutes irradiation. In this period, the sample was seemed to be under nucleation and ripening process. Above 30 minutes irradiation, the sample was under fragmentation process of formed NPs, in which mean-particle size decreased. Finally, mean particle size became 4 nm in diameter after 120 minutes irradiation for 30 mL metal ion solution. Interestingly, flow rate did not affect the NPs productivity. Moreover, productivities of NPs using a stationary and a flow system were 0.39 and 0.89 μg/s, respectively. These results were slightly better compared to that obtained by laser ablation in liquid (LAL) method. Furthermore, the proposed method has advantage of forming solid-solution alloy with tunable composition ratio and controllable size, which are difficult to be achieved by LAL method.

In the last part, the stability of metal and alloy NPs using nano-GO as a capping agent was investigated. Catalytic performance of the integrated material of NPs/rGO was also examined by methanol oxidation reaction (MOR) using cyclic voltammetry. It is well known that platinum NPs show excellent catalytic performance in MOR. However, its activity is easily poisoned by CO gas during reduction-oxidation (redox) reaction. To avoid the problem of CO poisoning on the Pt NPs surface, bimetallic alloy NPs is effective due to the synergistic catalytic effect in MOR. On the other hand, catalytic performance is significantly influenced by reactive surface area and dispersion state on a supporting material. Utilization of capping agent is commonly used to control not only the particle size but also the dispersion state of NPs. However, utilization of the capping agent requires additional purification step resulting in a complicated synthesis protocol. In this work, I proposed the use of nano-GO as a particle stabilizer in the integration process of metal or Au-Pt alloy NPs on rGO through two steps: First, nano-GO was simultaneously produced with metal or alloy NPs by fragmentation of GO through highly intense femtosecond laser irradiation in mixture solution of metal ions and GO. Fabricated NPs seemed to be immediately modified with nano-GO in the solution and then stabilized through steric effect. Secondly, the colloidal solution of synthesized metal or alloy NPs capped with nano-GO was mixed with GO solution, and then the mixture was irradiated by fs laser with moderate laser power to produce an integrated material of NPs/rGO. The optimal laser condition for NPs/rGO formation was 5-6 mJ of laser pulse energy and 100 Hz of repetition rate for 45 minutes irradiation. Mixture solution was composed of 2.5×10^{-4} M metallic ions and 10 v/v% of GO solution (7.5×10^{-6} g/mL). As a result, the size distribution profile obtained from TEM images showed well-dispersed small particles with the mean size of less than 6.5 nm on the rGO. Catalytic activity of this composite catalyst in MOR process was evaluated using cyclic voltammetry. Although the catalyst had no response in acidic solution (H_2SO_4/CH_3OH), clear-current peaks were observed in alkali (KOH/CH_3OH) solution. Even though the number of particles was very small (4.5×10^{17} particles in 27 mL of water), catalytic effect in MOR was clearly observed as a strong peak around -0.17V with about 3.5 μA of current.

論文審査結果の要旨

グラフェンは多くの優れた特性を有していることから、新しい素材として期待されており、世界的に活発な研究が行われている。なかでも触媒活性を有する貴金属ナノ粒子との複合化材料の開発は、触媒活性や担持効率の向上の観点から、その実現が強く望まれている。本論文は、フェムト秒パルスを水溶液中に照射することによって生じる還元作用を利用して、酸化グラフェンの還元と、金－白金合金微粒子の合成を行い、さらにこれらの複合化と触媒活性の測定を行ったものである。

第１章では、グラフェンと酸化グラフェンの構造、合成法と特性および金属と合金ナノ粒子の安定化、組成制御と合成法について述べている。

第２章では、フェムト秒レーザーによる還元型酸化グラフェンとナノ粒子の合成機構と実験方法、材料の評価方法について述べている。

第３章では、水中に分散した酸化グラフェンにフェムト秒レーザーを照射して生じる還元作用によって還元型酸化グラフェンを合成できることを見出し、最適なレーザー照射条件を求めるとともに、還元型酸化グラフェンが形態学的および電気特性ともに優れていることを明らかにしている。

第４章では、フェムト秒レーザー照射による金属イオン還元に基づく金属ナノ粒子合成の効率向上のために、試料水溶液のフローシステムを構築し、貴金属ナノ粒子合成におけるフローレートや微粒子のサイズおよびサイズ分布への影響を実験的に明らかにし、フローシステムの有用性を実証している。

第５章では、酸化グラフェン自体をキャッピング材として用いる方法の提案と実験的検討を進め、金－白金合金ナノ粒子の微細化と安定化を実現し、また還元型グラフェンへの担持による複合材料を作製し、そのメタノール酸化反応に対する優れた触媒活性を明らかにした。

第６章は総括である。

以上要するに、本研究は、水溶液のフェムト秒レーザー照射による還元作用を利用して、酸化グラフェンの還元と金－白金合金ナノ粒子の合成を行い、さらにそれらの複合材料の作製と特性評価を行ったものである。これらの成果は、酸化グラフェンと貴金属合金ナノ粒子との複合材料の重要性を明らかにしたものであり、材料工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。